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About Water Activity

What is water activity?
Water activity is derived from fundamental principles of thermodynamics and physical chemistry. As a thermodynamic principle there are requirement in defining water activity that must be met. These requirements are; pure water (a_w = 1.0) is the standard state, the system is in equilibrium, and the temperature is defined.

In the equilibrium state:

$$\mu = \mu_o + RT \ln (f/f_o)$$

where: μ (J mol^{-1}) is the chemical potential of the system i.e. thermodynamic activity or energy per mole of substance; μ_o is the chemical potential of the pure material at the temperature T (°K); R is the gas constant (8.314 J mol^{-1} K^{-1}) ; f is the fugacity or the escaping tendency of a substance; and f_o is escaping tendency of pure material (van den Berg and Bruin, 1981). The activity of a species is defined as a = f/f_o. When dealing with water, a subscript is designated for the substance,

$$a_w = f/f_o$$

a_w is activity of water, or the escaping tendency of water in system divided by the escaping tendency of pure water with no radius of curvature. For practical purposes, under most conditions in which foods are found, the fugacity is closely approximated by the vapor pressure (f $\simeq$ p) so;

$$a_w = f/f_o \simeq p/p_o$$

Equilibrium is obtained in a system when μ is the same everywhere in the system. Equilibrium between the liquid and the vapor phases implies that μ is the same in both phases. It is this fact that allows the measurement of the vapor phase to determine the water activity of the sample.

Water activity is defined as the ratio of the vapor pressure of water in a material (p) to the vapor pressure of pure water (p_o) at the same temperature. Relative humidity of air is defined as the ratio of the vapor pressure of air to its saturation vapor pressure. When vapor and temperature equilibrium are obtained, the water activity of the sample is equal to the relative humidity of air surrounding the sample in a sealed measurement chamber. Multiplication of water activity by 100 gives the equilibrium relative humidity (ERH) in percent.

$$a_w = p/p_o = ERH\ (\%)\ /\ 100$$

Water activity is a measure of the energy status of the water in a system. There are several factors that control water activity in a system. Colligative effects of dissolved species (e.g. salt or sugar) interact with water through dipole-dipole, ionic, and hydrogen bonds. Capillary effect where the vapor pressure of water above a curved liquid meniscus is less than that of pure water because of changes in the hydrogen bonding between water molecules. Surface interactions in which water interacts directly with chemical groups on undissolved ingredients (e.g. starches and proteins) through dipole-dipole forces, ionic bonds (H_3O^+ or OH^-), van der Waals forces (hydrophobic bonds), and hydrogen bonds. It is a combination of these three factors in a food product that reduces the energy of the water and thus reduces the relative humidity as compared to pure water. These factors can be grouped under two broad categories osmotic and matric effects.

Due to varying degrees of osmotic and matric interactions, water activity describes the continuum of energy states of the water in a system. The water appears "bound" by forces to varying degrees. This is a continuum of energy states rather than a static "boundness". Water activity is sometimes defined as "free", "bound", or "available water" in a system. Although these terms are easier to conceptualize, they fail to adequately define all aspects of the concept of water activity.

Water activity is temperature dependent. Temperature changes water activity due to changes in water binding, dissociation of water, solubility of solutes in water, or the state of the matrix. Although solubility of solutes can be a controlling factor, control is usually from the state of the matrix. Since the state of the matrix (glassy vs. rubbery state) is dependent on temperature, one should not be surprised that temperature affects the water activity of the food. The effect of temperature on the water activity of a food is product specific. Some products increase water activity with increasing temperature, others decrease aw with increasing temperature, while most high moisture foods have negligible change with temperature. One can therefore not predict even the direction of the change of water activity with temperature, since it depends on how temperature affects the factors that control water activity in the food.

As a potential energy measurement it is a driving force for water movement from regions of high water activity to regions of low water activity. Examples of this dynamic property of water activity are; moisture migration in multidomain foods (e.g. cracker-cheese sandwich), the movement of water from soil to the leaves of plants, and cell turgor pressure. Since microbial cells are high concentrations of solute surrounded by semi-permeable membranes, the osmotic effect on the free energy of the water is important for determining microbial water relations and therefore their growth rates.

Why is water activity important?
Water activity (a_w) is one of the most critical factors in determining quality and safety of the goods you consume every day. Water activity affects the shelf life, safety, texture, flavor, and smell of foods. It is also important to the stability of pharmaceuticals and cosmetics. While temperature, pH and several other factors can influence if and how fast organisms will grow in a product, water activity may be the most important factor in controlling spoilage. Most bacteria, for example, do not grow at water activities below 0.91, and most molds cease to grow at water activities below 0.80. By measuring water activity, it is possible to predict which

microorganisms will and will not be potential sources of spoilage. Water activity--not water content--determines the lower limit of available water for microbial growth. In addition to influencing microbial spoilage, water activity can play a significant role in determining the activity of enzymes and vitamins in foods and can have a major impact their color, taste, and aroma. It can also significantly impact the potency and consistency of pharmaceuticals.

Free water versus bound water.
Water activity describes the continuum of energy states of the water in a system. The water in a sample appears to be "bound" by forces to varying degrees. This is a continuum of energy states, rather than a static "boundness." Water activity is sometimes defined as "free", "bound", or "available water" in a system. These terms are easier to conceptualize, although they fail to adequately define all aspects of the concept of water activity. Water activity instruments measure the amount of free (sometimes referred to as unbound or active) water present in the sample. A portion of the total water content present in a product is strongly bound to specific sites on the chemicals that comprise the product. These sites may include the hydroxyl groups of polysaccharides, the carbonyl and amino groups of proteins, and other polar sites. Water is held by hydrogen bonds, ion-dipole bonds, and other strong chemical bonds. Some water is bound less tightly, but is still not available (as a solvent for water-soluble food components). Many preservation processes attempt to eliminate spoilage by lowering the availability of water to microorganisms. Reducing the amount of free--or unbound--water also minimizes other undesirable chemical changes that occur during storage. The processes used to reduce the amount of free water in consumer products include techniques like concentration, dehydration and freeze drying. Freezing is another common approach to controlling spoilage. Water in frozen foods is in the form of ice crystals and therefore unavailable to microorganisms for reactions with food components. Because water is present in varying degrees of free and bound states, analytical methods that attempt to measure total moisture in a sample don't always agree. Therefore, water activity tells the real story.

Controlling non-enzymatic reactions.
Foods containing proteins and carbohydrates, for example, are prone to non-enzymatic browning reactions, called Maillard reactions. The likelihood of Maillard reactions browning a product increases as the water activity increases, reaching a maximum at water activities in the range of 0.6 to 0.7. In some cases, though, further increases in water activity will hinder Maillard reactions. So, for some samples, measuring and controlling water activity is a good way to control Maillard browning problems.

Slowing down enzymatic reactions.
Enzyme and protein stability is influenced significantly by water activity due to their relatively fragile nature. Most enzymes and proteins must maintain conformation to remain active. Maintaining critical water activity levels to prevent or entice conformational changes is important to food quality. Most enzymatic reactions are slowed down at water activities below 0.8. But some of these reactions occur even at very low water activity values. This type of spoilage can result in formation of highly objectionable flavors and odors. Of course, for products that are thermally treated during processing, enzymatic spoilage is usually not a primary concern.

Measuring water activity

There is no device that can be put into a product to directly measure the water activity. However, the water activity of a product can be determined from the

relative humidity of the air surrounding the sample when the air and the sample are at equilibrium. Therefore, the sample must be in an enclosed space where this equilibrium can take place. Once this occurs, the water activity of the sample and the relative humidity of the air are equal. The measurement taken at equilibrium is called an equilibrium relative humidity, or "ERH".

Choosing a measurement tool.
Two different types of water activity instruments are commercially available. One uses chilled-mirror dewpoint technology while the other measures relative humidity with sensors that change electrical resistance or capacitance. Each has advantages and disadvantages. The methods vary in accuracy, repeatability, speed of measurement, stability in calibration, linearity, and convenience of use.

Which sensor works best for measuring the water activity of products? The major advantages of the chilled-mirror dew point method are accuracy, speed, ease of use and precision. The range of Decagon's AquaLab, for example, is from 0.030 to $1.000a_w$, with a resolution of $\pm0.001a_w$ and accuracy of $\pm0.003a_w$. Measurement time is typically less than five minutes. Capacitance sensors have the advantage of being inexpensive, but are not typically as accurate or as fast as the chilled-mirror dewpoint method. Capacitive instruments measure over the entire water activity range—0 to 1.00 a_w, with a resolution of $\pm0.005a_w$ and accuracy of ±0.015. Some commercial instruments can measure in five minutes while other electronic capacitive sensors usually require 30 to 90 minutes to reach equilibrium relative humidity conditions.

Chilled-mirror theory.
In chilled mirror dewpoint instruments, a sample is equilibrated within the headspace of a sealed chamber containing a mirror, an optical sensor, an internal fan, and an infrared temperature sensor. At equilibrium, the relative humidity of the air in the chamber is the same as the water activity of the sample. A thermoelectric (Peltier) cooler precisely controls the mirror temperature. An optical reflectance sensor detects the exact point at which condensation first appears. A beam of infrared light is directed onto the mirror and reflected back to a photodetector, which detects the change in reflectance when condensation occurs on the mirror. A thermocouple attached to the mirror accurately measures the dew-point temperature. The internal fan is for air circulation, which reduces vapor equilibrium time and controls the boundary layer conductance of the mirror surface. Additionally, a thermopile sensor (infrared thermometer) measures the sample surface temperature. Both the dew point and sample temperatures are then used to determine the water activity. During a water activity measurement, the instrument repeatedly determines the dew-point temperature until vapor equilibrium is reached. Since the measurement is based on temperature determination, calibration is not necessary, but measuring a standard salt solution checks proper functioning of the instrument. If there is a problem, the mirror is easily accessible and can be cleaned in a few minutes.

Capacitive sensor theory
Some a_w instruments use capacitance sensors to measure water activity. Such instruments use a sensor made from a hygroscopic polymer and associated circuitry that gives a signal relative to the ERH. The sensor measures the ERH of the air immediately around it. This ERH is equal to sample water activity only as long as the temperatures of the sample and the sensor are the same. Since these instruments relate an electrical signal to relative humidity, the sensor must be

calibrated with known salt standards. In addition, the ERH is equal to the sample water activity only as long as the sample and sensor temperatures are the same. Some capacitive sensors need between 30 and 90 minutes to come to temperature and vapor equilibrium. Accurate measurements with this type of system require good temperature control.

Evaluating Instrumentation

When evaluating water activity measurements, precision and accuracy are, of course, important considerations. But equally important to consider is how susceptible the sensor is to contamination and how frequently calibration is required. Also, when comparing water activity instruments, be sure to evaluate precision and accuracy over the entire range of water activities most commonly found in your specific products.

Water activity--accepted and approved

For many products, water activity is an important property. It predicts stability with respect to physical properties, rates of deteriorative reactions, and microbial growth. The growing recognition of measuring water activity in foods is illustrated by the U.S. Food and Drug Administration's incorporation of the water activity principle in the definition of non-potentially hazardous foods (Potentially Hazardous Foods means food with a finished equilibrium pH greater than 4.6 and a water activity greater than 0.85). They use this and other criteria to determine whether a scheduled process must be filed for the thermal destruction of Clostridium botulinum (Botulism). In the past, measuring water activity of foodstuffs was a frustrating experience. New instrument technologies have vastly improved speed, accuracy and reliability of measurements.

Food Product

Maintaining Vigilance Over Quality

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By: Carol J. Vandell
Contributing Editor

With greater emphasis being placed on the food industry to provide safe and nutritious foods, it's become increasingly important to monitor those products from the beginning of the production phase, to storage and handling, and finally to the consumer.

Hazard Analysis Critical Control Points (HACCP) implementation has become important to most facets of food production, whether involving meats, eggs, vegetables, beverages or processed foods. Also, more companies require that new suppliers and co-packers go through vendor certification programs. Therefore, chemical, microbial and physical testing of products should be conducted throughout production. The finished product should be tracked and monitored during storage and transit to ensure it is sold to consumers at its peak quality.

Many instruments and systems help food companies keep track of product quality. Much of the collected data can be downloaded into computer-generated reports where technicians can spot small problems before they become big problems, and adjust things accordingly. This ultimately saves time and money should a company need to reject or recall large amounts of product.

Gauging color

A product's appearance greatly influences its salability. If a product's color is faded or dull, a consumer might interpret this as a sign of excessive age. If a bakery item is darker than normal, consumers might think it's been overbaked. These initial impressions can either make or break a sale, so it's important to include measurements for color as part of a product-testing program, as these objective measurements will help quantify the color variances and differences.

A specific color can be measured numerically by creating a three-dimensional coordinate system scale for hue (red, yellow, green, blue, etc. that form the color wheel), lightness (brightness or darkness), and saturation (vivid or dull colors). The assigned values, L*a*b*, view color in a a similar manner to which the human eye sees color, with L* measuring light-to-dark color components, a* measuring the red-green scale, and b* measuring the yellow-blue scale. L*a*b* values are calculated from the tristimulus values (X, Y, Z), which are the backbone of all color mathematical models. The location of a color in the color space is defined by these values.

Color difference meters. This type of meter typically measures the color of a product on a specific scale to ensure a consistent product appearance time after time. For example, Minolta Corporation, Ramsey, NJ, manufactures a baking contrast meter (model BC-10) that measures the color of baked, fried and processed foods, as well as ingredients. This meter uses a scale of 0.01 to 5.25, the lowest reading being raw product, and the highest reading being a dark product. Personnel who use this type of meter need to define an acceptable scale number for their product and use this as a standard. All further samples taken are compared with the standard reading and determined acceptable or unacceptable. This type of instrument also can be used as a processing tool for new products - determining shades of lightness/darkness concerning bake or fry time and what temperature settings to use.

Colorimeters. This type of instrument looks at a sample as it appears under daylight by using a pulsed xenon arc lamp that provides constant output for each reading. The lamp illuminates test samples and the light reflected back from the test surface is color-analyzed to give an L*a*b* reading. The reading will tell how much the sample differs from the standard. However, it doesn't provide detail-specific information that would help the analyst determine how to correct color problems. Colorimeters are commonly used to help QA personnel determine if a product is out of the color specification range. Researchers use it to track color changes of product over time. This type of information is valuable because it provides packaging and storage information that leads to process improvements.

Spectrophotometers. Spectrophotometers can look at a sample under 11 different illuminants. You can look at an object and determine the way the color will look under daylight, fluorescent, cool white, to northern sky light. It will then give the color readings in various color spaces and also will provide the spectral curves. "A spectrophotometer gives you the most absolute measurement as far as accuracy and repeatability are concerned," says Maria Repici, marketing manager, Minolta Corporation. "If you want to get the same color time after time, and you want to be able to match that color or re-create that color, and if you have very strict parameters or tolerances that you're meeting in order to control the color, you would want to use the spectrophotometer." She also emphasized the importance of using spectrophotometers that have a high degree of inter-instrument agreement when you have manufacturing facilities worldwide. This would provide absolute color-matching within the company to provide a consistent product.

Online inspection

Some valuable tools for building quality are online inspection systems, which range from metal detectors and X-ray units to machine vision systems, to name only a few. These machines replace the subjective judgments of human inspectors with the objectivity of machines. They have the ability to examine large quantities of product at high speed to detect rejects. They also have high sensitivity levels, so they reject only the predetermined defective product, which generally results in greater yield of acceptable product.

Metal detectors. The internal workings of metal detectors now employ sophisticated technologies, such as digital signal processing to quickly differentiate the signals of conductive foodstuffs from that of ferrous (iron, tin, steel), nonferrous (aluminum, lead, copper), and stainless steel metal contamination. Ferrous contamination is magnetic as well as a good electrical conductor. Nonferrous metals are nonmagnetic, but serve as

good electrical conductors. Both of these categories are easy to detect. Stainless steel presents a problem because some grades are magnetic and other grades are not. This limits the metal detector's sensitivity when trying to detect this type of metal.

Metal detectors are comprised of two parts, the electronics and the search head. The search head inspects the product as it passes through the aperture, where it is subjected to an oscillating electromagnetic field called the "search field." A coil arrangement inside the search field is electrically balanced and connected with a combined output of zero. When a magnetic or conductive object passes into the search field, the net output is greater than zero, and the product is rejected.

"Ninety-five percent of metal detection is done on the individual product rather than on the case," says Scott Patterson, vice president, marketing, Cintex of America Inc., Kenosha, WI. "The smaller the distance that the aperture is from the product being tested, the greater the sensitivity will be.

"When checking full cases, the height adjustment needed to accommodate the box enlarges the aperture, which makes the machine less sensitive," Patterson says. "Also, many times, corrugate boxes are made from recycled materials which contain trace pieces of metal. This will cause the machine to reject the box, when the contamination is actually coming from the box and not from the actual product."

A system also exists that will allow metal detection when the foods are packaged in foil bags, aluminum trays or aluminum pans. The unit works identically to the standard metal detection, although the detection field is set up to disregard nonferrous and stainless-steel contamination. This is achieved by using a direct current signal that has a very low frequency.

X-ray machines. These machines can be used to detect contaminated (with rocks, glass, plastic, metals and bone), missing and even misaligned package contents directly on the production line. They scan the product with X-ray. If the contents do not conform to pre-determined standards, the product can be removed either manually or automatically with the use of rejection jets.

Machine vision systems. Processors of french fries, raisins and other fruits, vegetables, cereals and candy are reaping tremendous benefits from machine vision technology, which improves quality, consistency, yield and efficiency by sorting and removing defective products from the continuous product stream. "The machine vision industry has gotten more sophisticated. As the food-processing industry became more sophisticated, the demand for increased performance has driven our technology," says Karen McQueen, marketing communications manager, SRC Vision, Inc., Medford, OR.

Machine vision systems are able to target obvious defects (such as unwrapped candy or burnt, discolored product) or otherwise undetectable defects (such as fruit pits or embedded stems in raisins) faster and more consistently than human sorting. They do this by combining camera technology with customer-specific, product-illumination lamps that will fit their application, and integrating this with intuitive computer software. Once the computer has identified and selected articles as defective, either by color, shape or size, they are automatically ejected in-flight by precise jets of filtered, compressed air. High-speed, black-and-white scanning cameras are typically used for products in which the color of the defect is dramatically different from the acceptable color of the product, such as with

french fries. High-speed, color-scanning cameras are used when the defect defect is a similar hue or color to the product being monitored, such as with string beans where the stem and the bean are basically the same color. Defect levels need to be established by the food processor as this will critically affect their product yield. There are system-compatible analytical machines available to use for analyzing production data.

Taking the temperature

Time and temperature represent two critical factors in the fight against pathogenic microorganisms that can contaminate a food product being produced, transported or stored. In fact, monitoring and recording temperatures during heating, cooling, transportation and storage is crucial in certifying that foodstuffs have been handled in accordance with HACCP standards. Tracing of temperatures using electronic means protects the consumer and the industry. It is a QA tool that should become an integral part of a company's total QC plan. Instruments available are rugged, often portable, tamper-proof, waterproof, affordable and easy to use, and can interface with software for easy downloading of data. They can be programmed to take temperatures at certain intervals, sound alarms or change color when out-of-range conditions occur, and keep a permanent record of the temperature conditions.

Data loggers. These devices can take continuous temperature readings at at various points during processing, storage and shipment. One such device, the TempTale unit available from Sensitech Inc., Beverly, MA, can be secured onto a pallet of goods, or to the interior wall of a truck at the start of a trip, and removed when the goods reach their final destination. Temperature information then can be downloaded and analyzed to determine whether the shipment stayed within prescribed temperature ranges. Shipments can be accepted or denied based on the data obtained. Also, data loggers are available that can be used in baking ovens, coolers, dryers and freezers. Temperatures can be taken inside an oven, as well as inside product going through those ovens. This information is then downloaded and can be used to solve a variety of QC, maintenance and product development issues.

Time-temperature integrator (TTI) tags. TTI tags incorporate a color indicator with multiple dots that change when temperature or shelf-life requirements have been exceeded. The tags can be matched to the storage requirements of a particular foodstuff, because the color shifts are affected by an enzymatic reaction chosen specifically for that product. The tags can be placed on individual cases or pallets instead of being hung inside of a truck - an important consideration when multiple deliveries are made by one vehicle or when the product is being shipped by multiple modes of transportation.

Handheld noncontact infrared thermometers. All that's needed is to point, shoot and read the temperature. Infrared thermometers feature a laser circle that outlines the spot size being measured at any distance. They offer two key application benefits over conventional thermometers. First, they can be used to replace contact temperature measurement systems, such as probes, that can potentially contaminate the source. Secondly, in large food storage areas, such as walk-in freezers and refrigerators, where a single thermometer is often used to monitor the environment, the infrared thermometer affords the user the ability to spot-check various "targets" for a more complete assessment of temperatures throughout the location. They enable users to take even more readings than usual because they decrease the time it takes when using conventional thermometers.

"The National Environmental and Health Association, along with Raytek Corporation and other infrared manufacturers, is working with legislators in Washington, D.C., regarding regulations that would include spot-checking with infrared," says Michele Reutzel, marketing communications specialist, Raytek Corporation, Santa Cruz, CA. "Infrared thermometers would play a very important part in every HACCP program."

Temperature-indicating labels. Temperature labels permanently record maximum interior or exterior temperatures of products during processing, storage and shipment. They're inexpensive, easy to use, and can be utilized as a permanent temperature record. The labels are formulated to react within a few seconds when the rated temperature is reached. The various single and multi-temperature labels are generally rated within an overall temperature range of 90°F to 500°F (32°C to 260°C). As each section of a label reaches its rated temperature, that section responds with a sharply defined color change from white to black, leaving the printed temperature clearly visible. They can be used in areas such as ovens, curing and sterilizing chambers, ships' holds, as well as inside processed foods. They have a shelf life of two years when stored at room temperature, and come in various temperature ranges.

Remote data loggers. A completely different technology for tracking temperatures of food products during domestic or worldwide transportation and storage is available from Measurement Dynamics L.L.C., West Warwick, RI. Not only are temperature conditions recorded, but the actual physical location of the product is identified, even while the product is in transit. The temperature-recording equipment is linked to communications equipment using global-positioning satellite telemetry. This can locate a shipment anywhere in the world. After determining where the product is, producers can save satellite charges by using cellular phones to download information about what conditions have existed within the cargo box.

Water activity

Water activity (Aw) is equilibrium relative humidity with the decimal point moved two places to the left (example: 100% humidity = Aw 1.00). At the 100% humidity level, water is available at zero tension. Aw is defined as the free, unbound water present in food and food products. It influences bacterial growth, non-enzymatic browning, lipid oxidation, degradation of vitamins, enzymatic reactions, protein denaturation, starch gelatinization and starch retrogradation. This is why it is important to measure a food product's Aw. It provides an idea of how a food system is reacting to the water present in the system (including moisture migration and susceptibility to pathogens). Knowing Aw values also can serve as a valuable tool when determining drying times for dehydrated product and determining product shelf life.

The food sample to be analyzed is put into a sample cup, then put into the the meter for reading. The water in the sample diffuses into the atmosphere above the cup, and the water molecules in the atmosphere diffuse into the sample. Eventually, the two systems come to a state of equilibrium, where the diffusion is equal. This point is called equilibrium relative humidity and is used to calculate the Aw of the sample. This reading is generally taken at room temperature, and can range from 0.100 to 1.000. Decagon Devices, Inc., Pullman, WA, manufactures a model that can measure Aw values within five minutes or less by utilizing an internal fan system that speeds up the equilibration time. This is an important advantage when multiple samples need to be analyzed. The company carries a meter that controls the temperature of the sample using a

circulating water bath, says Anthony Fontana, Jr., Ph.D., applications engineer, Decagon Devices, Inc. This type of system is used to determine the Aw value at a specific temperature (other than room temperature) to satisfy corporate internal regulations, such as readings at 25°C. It also is useful for temperature studies as well as accelerated shelf-life studies.

In today's environment, it's easy for a good product to go bad. But technology has brought us a wide variety of detection instruments to help keep food products on the straight and narrow.

Carol Vandell is a technical writer and food-safety consultant. She has a bachelor's degree in food technology and 11 years experience in the food industry. Her specialties include QA/QC, R&D and food-safety fields.

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Moisture Migration and Control in Multi-Domain Foods

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Abstract

Control of initial moisture content and moisture migration is critical to the quality and safety of multi-domain foods. Moisture loss or gain from one region or food component to another region will continuously occur in order to reach thermodynamic equilibrium with the surrounding food components and the environment. Two main factors influencing the amount and rate of moisture migration are water activity equilibrium (thermodynamics) and factors affecting the diffusion rate (dynamics of mass transfer). Adding an edible layer between domains, changing the water activity of the food ingredients, changing the effective diffusivity of the water, and changing the viscosity (molecular mobility) in the entrapped amorphous phases are several means to control the water migration between domains in food systems.

Introduction

Control of initial moisture content and moisture migration is critical to the quality and safety of foods. Ideally, food manufacturers develop products with defined moisture contents to produce a safe product with optimum shelf-life. Quality and safety factors that the manufacturer must consider are microbial stability, physical properties, sensory properties, and the rate of chemical changes leading to loss of shelf-life. These above factors all depend on the amount of moisture and the water activity of each domain in a multi-domain food system. A multi-domain system can be at the macromolecular or molecular level. Examples of macromolecular multi-domain system are dry cereal with semi-moist raisins, frozen pizza crust with sauce, ice cream in a cone, a pastry with a fruit filling, chocolate or hard candy with liquid centers, a cheese and cracker snack, and the crust and crumb of a loaf of bread right after baking. Examples of the molecular level multi-domain systems are water within a starch granule or water in different regions (starch, protein) in a baked product.

Multi-domain systems are dynamic. Moisture loss or gain from one region or food component to another region will continuously occur in order to reach thermodynamic equilibrium with the surrounding food components and the environment. Several factors influence the amount and rate of moisture migration in multi-domain foods. Two main factors are water activity equilibrium (thermodynamics) and factors effecting the diffusion rate (dynamics of mass transfer). To control this migration, several principles can be utilized to inhibit the change in moisture including adding an edible layer between domains, changing the water activity of the food ingredients, changing the effective diffusivity of the water, and changing the viscosity (molecular mobility) in the entrapped amorphous phases.

Importance of moisture control to stability

Changes in the amount of moisture of a multi-domain food system can affect the physical and chemical composition along with the safety and shelf-life of a food. Many physical and chemical changes from moisture migration can be related to the glass transition. To gain an understanding of how glass transition affects physical and chemical reactions in foods, a brief description is given below.

Multi-domain regions in solid foods can exist in either a thermodynamically stable crystalline state or in an amorphous state, which is not at true equilibrium. Regions that are in the amorphous state can exist in a rubbery or glassy state. Amorphous materials exhibit a property called the glass transition temperature (T_g) which is a second order transition. When the material changes from the glassy state to the rubbery state or vice versa there are changes in thermodynamic properties, molecular mobility, dielectric constant, and mechanical properties[1]. This transition is influenced by plasticization by water or other ingredients, the molecular weight of ingredients and the amount and type of bonding interactions[2]. Thus, if a multi-domain region gains or loses moisture, it may move between the rubbery and glassy states.

The amount of plasticizer, water, along with the temperature determines what state the region is in. This can best be seen by a state diagram as shown in Figure (1). The state diagram defines the moisture content and temperature region at which a food domain is glassy, rubbery, crystalline, frozen, etc. State diagrams are particularly useful in the characterization of the physical state of sugars and the water content dependence of transition temperatures[4].
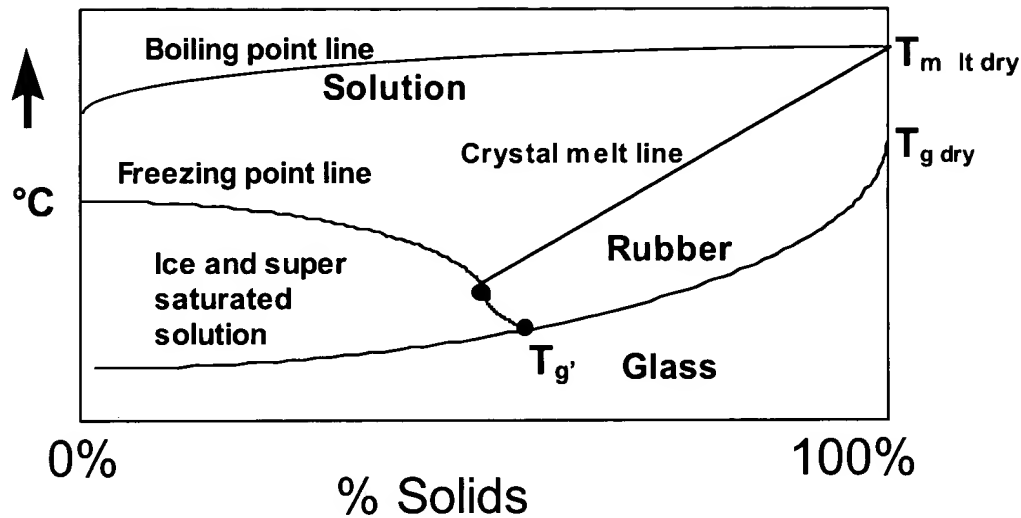
Figure 1: State Diagram (Adapted from Ref. 3)

T_g, **glass transition**

$T_{melt\,dry}$ **(melting temperature of crystal state at zero moisture)**

$T_{g\,dry}$ **(glass transition temperature of dry glassy state)**

$T_{g'}$ **(glass transition temperature of maximally concentrated frozen state)**

Water activity (a_w), instead of percent moisture is many times a better indicator of the safety and quality of foods[5]. Water activity is related to equilibrium relative humidity (ERH) as shown in Equation 1 and is a function of water content:

$$\%ERH = a_w \bullet 100 = \frac{p}{p_o} \bullet 100 \qquad\qquad (1)$$

where p = actual pressure of water in the sample and p_o = vapor pressure of pure water. Water content verses a_w at constant temperature can be plotted to gain more understanding of how much water can be gained or lost by a food system before the food becomes unacceptable. This plot is called a moisture sorption isotherm (Figure 2).
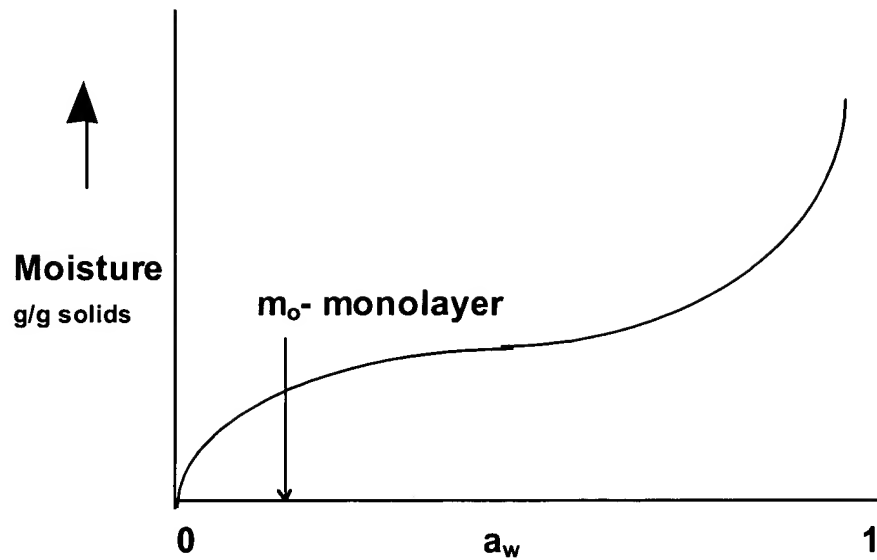
Figure 2 Moisture sorption isotherm at contsant temperature (m_o represents the optimal moisture for maximum storage stability in the dry state) (Adapted from Ref. 37)

Effects on physical stability

Physical factors influencing the shelf-life of food systems include crystallization, stickiness , and texture. The rate of crystallization increases as moisture increases thus limiting the shelf-life[6]. The rate of crystallization also increases as a function of temperature above the glass transition temperature $(T-T_g)$ as long as the aqueous system is saturated with the diffusing molecules[7]. Below the T_g, crystallization and other reactions occur very slowly because the food in the glassy state has a very high viscosity of about 10^{12}Pa-sec[8]. Molecular movement is decreased substantially at this high viscosity except for small molecules such as oxygen or water vapor that can diffuse through larger pores. Above the T_g, viscosity decreases significantly. This decrease allows for the increase of molecular movement of other molecules and thus allows reactions to occur more freely. Since amorphous sugars are very hygroscope, if they are exposed to high humidities in the rubbery state, crystallization will occur resulting in a coarse and grainy texture[7]. Fondants, cream fillings, fudge, and jams are often used as a filling for many baked products. Texture and the overall quality of these products can be related to crystallization of sugars[9]. Also of importance is the rapid crystallization of sugar in some high moisture cookies. For example, chocolate chip cookies change from a soft desired texture into a hard undesirable state because of the sugar crystallization over time[10]. While controlled sugar crystallization is desired in some products (caramel, creams, and fondant), prevention of crystallization is required in others (marshmallows and ice cream)[9]. There are several problems that the senior author worked on with food companies in which sugar crystallization of a high moisture pastry in a water impermeable package led to an increase in a_w of the surrounding regions followed by mold growth making the product unacceptable.

At a critical temperature and moisture content, powders become sticky and thus can cake together. Water begins to bridge the powder granules together[11]. This occurs at a temperature at above 30-70°C above the glass transition of the powder[12,13]. In multi-domain foods, problems can occur when trying to add higher a_w ingredients to seasoning packets or adding ingredients to powdered systems that are hygroscopic.

Both crystallization and stickiness of food systems can have a negative effect on consumer acceptance of texture. Also, the crispy/hard or soft/rubbery texture can influence consumers acceptance of a multi-domain system. When a crispy cracker of low water activity is put into contact with cheese, jam, or a fruit paste of high water activity, it absorbs water and becomes rubbery[14]. It goes from point A to point B as shown in Figure (3). Cereals with semi-dried fruits begin to pick up water and become less crisp above an a_w greater than 0.5[15]. The same alteration occurs in various multi-domain systems such as pizza crust with sauce[14] or a baked cone filled with ice cream[16]. Dry foods in a semi-permeable pouch that allows the influx of water vapor can show similar glass to rubber transitions. Crispness is lost if water is gained to reach an a_w above 0.35 to 0.50 for crisp snack foods like chips, saltine crackers, popped pop corn, and corn curls[17], 0.44 for puffed rice cakes[18], and 0.28 to 0.55 for breakfast cereals[19]. Crispness or crunchy texture is essential to the quality of a number of cereal and snack products. If the moisture content increases due to the absorption of water vapor or the mass transport of water from other domains, crispness is lost.
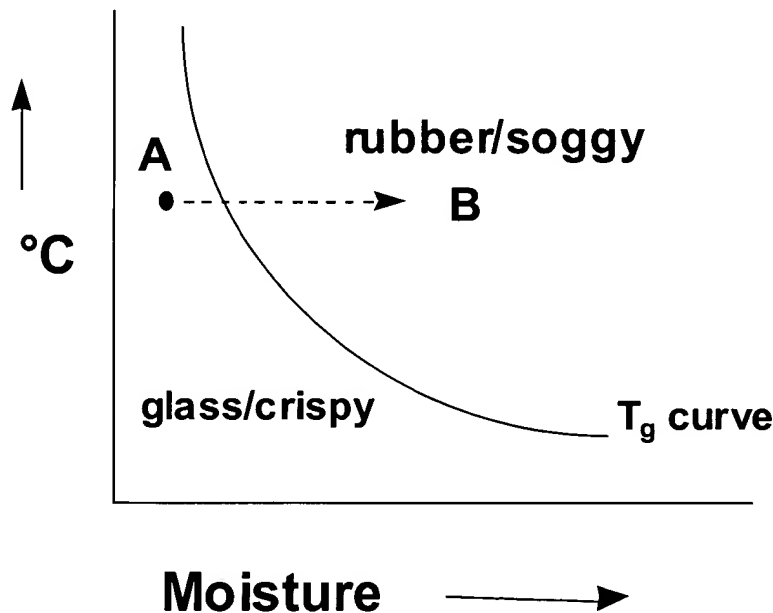
Figure 3 Hypothetical path in the state diagram for a crispy cracker absorbing water from the atmosphere at constant temperature, showing the crisp (A) to soggy (B) phase transition

When a crisp food is broken or crushed a characteristic sound is produced due to the brittle fracture of cell walls. These acoustic emissions have been used to qualify sensory crispness[20], and the less crispy materials produce less acoustic emission[21]. Nelson and Labuza[10] pointed out that dry cereals have a crisp texture in the glassy state, but plasticization by increasing water content or temperature may transfer the material to the rubbery state which causes sogginess. The results suggested that crispness, determined by sensorial and instrumental methods was lost as the T_g was depressed below ambient temperature as a result of water plasicization[4]. On the other hand, Kirby *et al.*[22] suggested that crispness is linked to fracture processes that are not necessarily linked to the glass transition. Some products depend on higher moisture contents to give a soft, moist texture such as raisins or other dried fruits. If these products lose moisture, then the products become hard and organoleptically unacceptable. The range for these dried fruits to become unacceptable is between a_w 0.5 to 0.7[23].

Effects on chemical reactions and microbial growth

Chemical reactions are also affected by moisture migration including lipid oxidation and non-enzymatic browning. Chemical reactions depend on the reacting compounds to come in contact with each other. The rate of non-enzymatic browning or oxidation depends on the ingredients in the system, the viscosity of the system, the dilution of reactants, and the mobility of the reactants. For enzymatic browning, the maximum reaction rate occurs somewhere between a_w 0.6-0.8[24]. For lipid oxidation, the rate increases both above and below the monolayer moisture content, thus prevention of moisture exchange is critical unless oxygen is excluded. Vacuum packaging, gas flushing or oxygen scavengers can be used, but for dry systems, scavengers will not work as well because they do not work well below 50% Relative Humidity (RH).

An increase in local moisture content as a result of moisture migration from one region to another can also cause microbial growth. In a multi-domain system, an increase of water content in the dry, low a_w region where no anti-microbial systems are present could allow for microbial growth. When the a_w goes above the lower growth limit of 0.60 for salt tolerant micro-organisms, 0.80 for most molds, about 0.87 for most yeast, and 0.91 for most pathogens, these microorganisms can begin to grow[25]. Microbial growth does not depend on water activity alone. Water activity is part of the hurdle effect in which several factors including pH, temperature of storage, thermal processing, preservatives, and competitive microflora contribute to increased resistance to microbial growth[26].

Factors affecting moisture migration

Thermodynamics

Water activity equilibrium (thermodynamics) and rate of diffusion (dynamics of mass transfer) are the two main factors influencing moisture migration in a multi-domain food. Multi-domain foods with regions formulated to different water activities cause the whole system to be in a non-equilibrium state. This will result in moisture migration from the higher water activity (higher chemical potential) to the lower a_w region and can result in undesirable changes in the system as described above.

The following example illustrates the condition of equilibrium. A dry cracker at an a_w of 0.30 is put in a sealed chamber with a relative humidity of 75% at 25°C. The initial moisture of the cracker is 3% (w/w) and thus it gains water at this high humidity. The final moisture after equilibration may be about 15% (w/w). In a separate chamber at the same conditions, a piece of cheese with an initial a_w of 0.95 is placed. Initially, the cheese has a

moisture content of 60% (w/w), but it looses moisture and after equilibration, it has a moisture content of about 25% (w/w). The final water activity of both the cracker and the cheese is 0.75 since they were both equilibrated at 75% RH (Equation 1). The a_w of the two systems is the same, although the moisture contents are very different (15% vs 25%). If the cheese and the cracker are now put together in a package, no moisture exchange occurs because they are in thermodynamic equilibrium.

Equation (2) relates the thermodynamic chemical potential of water vapor to the a_w:

$$\mu_v = \mu_0 + RT\ln\left(\frac{p}{p_o}\right) = \mu_0 + RT\ln a_w \qquad (2)$$

where μ_v = chemical potential in the sample of water vapor; μ_0 = chemical potential for pure water vapor; R = ideal gas law constant; T = Temperature; p = actual vapor pressure of water; and p_o = vapor pressure of water at saturation[27]. In the above example after equilibration for the water, $\mu_{cracker} = \mu_{chamber} = \mu_{cheese}$, and thus $a_{w\ cracker} = a_{w\ chamber} = a_{w\ cheese}$. In other words, the chemical potentials for the water are the same when the systems are brought to equilibrium at a constant relative humidity. Even though the percent moisture was not the same for the cheese and cracker, the water activities were the same, thus no change in moisture content occurs when they are put together unless other chemical reactions took place. This shows that one approach to prevention of moisture migration is eliminating the differences in water activity, thus maintaining the original condition. The question, of course, is whether one can achieve the desired textural characteristics at a high a_w. To our knowledge, no one has yet found a way to make a crispy cracker or potato chip (crisp) at a high moisture/a_w value.

The differences in vapor pressure of water between two regions also affects the rate to reach equilibrium. On a simplistic basis this can be described by Fick's First Law of diffusion (Equation 3):

$$\frac{dm}{dt} = \frac{k}{x}\left[p_1 - p_2\right] \qquad (3)$$

where dm/dt = amount of moisture exchange per unit of time, k = effective diffusivity of water, x = the path length for diffusion, p_1 = water vapor pressure in system 1, and p_2 = water vapor pressure in system 2. It is obvious that in real systems, as moisture is exchanged, the difference between p_1 and p_2 gets smaller and thus the rate of moisture transfer decreases. Thus, bringing the a_w of the systems as close as possible has some benefit.

Ingredients, capillary size and distribution and surface interactions are three factors contributing to the water activity of each food domain in a multi-domain system. To predict the effect on change of a_w by adding an ingredient, S, to the food, Raoult's law can be utilized (Equation 4).

$$a_w = \gamma_s X_{water} = \gamma_s\left(\frac{n_{water}}{n_{water} + n_{solute}}\right) \qquad (4)$$

Where γ_s = activity coefficient of ingredient S, X_{water} = mole fraction of water, and n = moles of solute and water in terms of kinetic units. Raoult's law is fairly good at predicting the a_w of a multi-domain component at high water activities or low solute content[28], but care must be taken in what water binding agent is added because of several limitations in Raoult's law. One such limitation is that Raoult's law does not consider the solubility limit of the agent in the food product. The formulator can theoretically produce foods at all a_w levels but from Table (1) this is not the case except for a liquid like glycerol or propylene glycol. Another limitation is the unknown degree to

which a compound behaves in a non-ideal fashion, i.e. γ generally is less than 1. A polyethylene glycol (PEG) solution at 4.25 Molal has a predicted water activity of 0.925 using Raoult's Law. However, as the molecular weight of PEG is increased, even at the same molality, it reduces the a_w more[29]. The nature of the molecule must be considered. For example, a one molal solution of NaCl behaves as a two molal solution of kinetic units because it ionizes into Na^+ and Cl^- ions. Looking at Table (2) one can see the variation in the molalities of different ingredients to achieve a given water activity.

Table 1: Common solutes and their properties for reducing a_w[a]

Solute	Maximum solubility in water (%)	a_w of saturated solution
Lactose	20	0.97
Glucose	47	0.92
KCl	27	0.86
Sucrose	69	0.86
Sorbitol	70	0.79
NaCl	26	0.75
Fructose	75	0.63
Glycerol	100	0.00

[a]Adapted from Ref 37

Table 2: molalities to achieve given a_w

a_w	Molality				
	Molality assuming ideal salt	NaCl	CaCl$_2$	Sucrose	Glycerol
0.995	0.28	0.15	0.10	0.27	0.28
0.960	2.31	1.20	0.77	1.92	2.21
0.850	9.80	4.03	2.12	5.98	8.47
0.75	18.5		3.00		14.8

One can modify Raoult's law to take into account the deviation from ideality as a function of concentration[28,30]. One such equation is the Norrish Equation (5) which accounts for multiple solutes and the concentration dependence of γ_s.

$$\ln a_w = \ln X_{water} + \frac{\sum_{i=1}^{j} K_i [X_i]^2}{\sum_{i=1}^{j} [X_i]^2} \left[1 - X_{H_2O}\right]^2 \tag{5}$$

where X_i = mole fraction of each solute i, K_i = correction factor derived from the activity coefficient for each solute, and j represents the number of solutes where:

$$\gamma_s = K_s (X_s)^2 \tag{6}$$

From a plot of measured log (a_w/X_{H2O}) vs $(X_s)^2$, the slope gives the value of K_s, thus γ_s can be determined as a function of concentration.

Chirife and Ferro-Fontan[31] studied the non-ideality of lactulose, sucrose, maltose, glucose and xylose solutions while Miracco et al.[32] studied lactose solutions. Both papers showed that a_w values predicted using Raoult's law were consistently lower than experimental a_w values. However, using the Norrish equation, the authors were able to calculate K for an optimum fitting with the experimental data. Other studies have found K values with good fit for other water activity lowering agents, i.e. salts[33], glycols[34], amino-acids[31], acids[33,35].

When adding water activity lowering substances one must consider the factors that limit the type and amount of the substance. A major limitation is flavor. Salt and carbohydrates are most often used but cause a salty flavor or sweeten the food too much simultaneously. Another limitation is that the toxicity of the molecule has to be considered, i.e. the water binding agent must be at a safe consumption level in the food. Recently, propylene glycol has been limited in the US as an a_w lowering agent because of its potential toxicity. Other limitations are consumer acceptance and physical and chemical reactions such as crystallization and Maillard browning during the storage of the modified product. About microbiological concerns, Gervais et al.[36] showed that the nature of the water binding agent used to depress a_w has a strong effect on the kinetics of bacterial spore germination.

Surface curvature as controlled by the capillary size and distribution is a second factor contributing to reduction of water activity. The water activity in a capillary structure can be related to the meniscus radius as follows (Equation 7):

$$\ln a_w = \frac{\Delta P \upsilon_m}{RT} \tag{7}$$

with $\Delta P = \Delta \rho\, gh = \dfrac{2\,\gamma \cos\theta}{r}$

where ΔP = pressure surface force or Poynting pressure; $\Delta \rho$ = [density water-density air]; g = gravitational constant; h = height of meniscus; γ = surface tension = 73 dynes/cm for pure water; r = capillary radius; v_m = liquid molar volume; and θ = wetting angle = 0 if perfectly wet. From the above equations, a smaller capillary radius has a greater suction pressure which reduces the effective vapor pressure and this decreases the water activity. For example

the a_w in a capillary of 0.01 µm radius is 0.90. Thus one could theoretically reduce the a_w of a food by engineering it to very small diameter pores. Unfortunately, no one has come up with a practical method to do this. Also, if the walls of the pores are too thick, the amount of water per unit volume will be very small.

A third factor contributing to reduction of water activity in a given region is the number and energy of the surface binding sites for water vapor. The more surface sites per gram of solids, the greater is the amount of water held at low a_w. In addition, the larger the excess enthalpy (Q_s) of interaction, the stronger the water is held. The BET (Equation 8) or the GAB (Equation 9) equations can be used to calculate the amount of water held as a function of a_w although the BET equation is limited to $a_w < 0.55$[37].

$$\frac{a_w}{(1-a_w)m} = \frac{1}{m_o c} + \left[\frac{c-1}{m_o c}\right]a_w \qquad (8)$$

$$m = \frac{m_o k_b c a_w}{(1-k_b a_w)(1-k_b a_w + k_b c a_w)} \qquad (9)$$

where m = the measured moisture at water activity = a_w; m_o = the monolayer moisture content (the optimal moisture content for maximum storage stability of a dry food); k_b = the GAB multi-layer constant; c = the isotherm temperature dependence coefficient (Equation 10)

$$c = e^{Qs/RT} \qquad (10)$$

where Q_s = excess enthalpy of sorption; R = gas constant; and T = temperature in °K.

When formulating a multi-domain food system, knowing the sorption isotherms for the components is beneficial for predicting the equilibrium a_{eq}. Iglesias and Chirife[38] have published a book of data on sorption isotherms for many food components. With a known isotherm equation for each component of a food, one can easily visualize the potential for transfer of moisture as seen in figure (4). If component A and B are mixed or placed in contact and they are originally at moisture of m_{Ai} and m_{Bi} with different water activities, moisture diffusion will occur until they reach the equilibrium a_{eq}. The mixture isotherm can be predicted from the following Equation (11):

$$m_i = f_A m_{Ai} + f_B m_{Bi} = \ldots \qquad (11)$$

where m_i = total moisture content for mixture at $a_w = a_i$; m_{Ai} = moisture content of component A at $a_w = a_i$; m_{Bi} = moisture content of component B at $a_w = a_i$; f_A = (g solids A)/(g total solids); f_B = (g solids B)/(g total solids). Thus by knowing the total moisture per gram of dry solids, one can then estimate the a_{eq} from the composite isotherm.
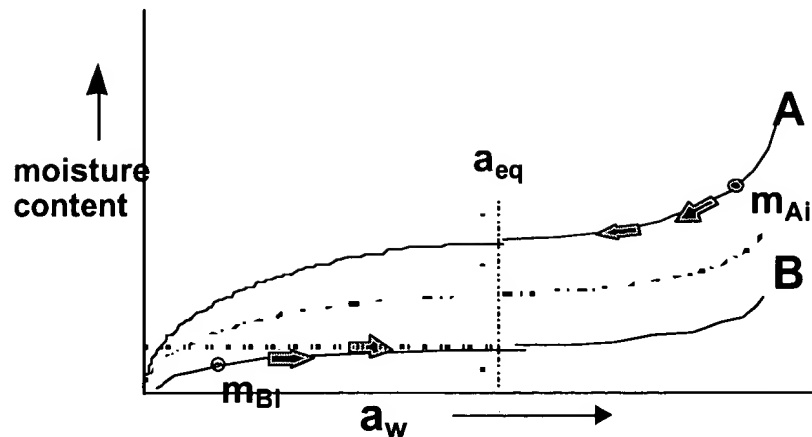
Figure 4: Moisture sorption isotherms (g water/g solids vs aw) for a two component system (A and B) showing the equilibration pathway to the same water activity

m_{Bi}, **Initial moisture for component B**

m_{Ai}, **Initial moisture for component A**

a_{eq}, **Equilibrium water activity**

Dynamics

Transfer between regions in a multi-domain system is mainly by diffusion. For multi-domain systems, determining the rates of diffusion within each domain is important to find which domain is rate limiting to moisture exchange. The two main factors controlling rate of diffusion of water are the local viscosity of the adsorbed aqueous phase of the system if diffusion occurs in the liquid state and the porous structure of the system for gaseous diffusion. The higher the local viscosity the less molecular movement as was noted with respect to rubbery and glassy states. The amount of water, the amorphous state of the food, the temperature, and the molecular weight of the ingredients all affect the local viscosity. Recent work using Nuclear Magnetic Resonance (NMR) and Magnetic Resonance Imaging (MRI) techniques[39] is leading to a better understanding of these factors. With MRI, actual rates of diffusion can be visualized during storage of a foods and the diffusivities can be estimated. Ruan and Litchfield[40] used MRI to follow the moisture mobility and distribution of corn kernels. Schmidt and Lai[41] reviewed the applications of NMR and MRI to study the water relations in foods. Umbach *et al.*[42] calculated water self-diffusion coefficients in starch-gluten-water systems by NMR. Heil *et al.*[43] studied water migration in baking biscuits by MRI. Jeffrey *et al.*[44] showed the capability of NMR microscopy to give radial profiles of water velocity in a model system. From these studies, MRI and NMR seem to be useful methods in gaining further understanding of the rates and paths of moisture migration. Theoretically, self-diffusion coefficients for water from NMR data are higher than the effective diffusion coefficients calculated from drying data. The differences between the macroscopic and microscopic data are presumed to be because of changes in sample dimension during the drying experiments as well as due to the impermeable barriers with the matrix[45]. Ruan and Addis (unpublished) have shown that adding a microparticularized fiber into pizza sauce reduces the NMR determined water mobility and this led to a slower diffusion rate of moisture into the crust during frozen storage.

As noted earlier, the diffusion region in the glassy state should behave as a more viscous material with slower diffusion than in the rubbery state. This can be modeled by the Boltzman Equation (12):

$$X^2 = \frac{k_b T \tau}{3\pi\eta D}$$

(12)

where x = vibrational space or diffusion distance in time τ, k_b = Boltzman constant, T = temperature °K, D = local effective diffusion coefficient, τ = characteristic time for molecular size movement, and η = local viscosity. If we compare the situation of a domain in the glassy state ($\eta = 10^{12}$ Pa sec) with that of the same domain in the rubbery state ($\eta = 10^6$ Pa sec) while keeping all other variables constant, then the time it takes for a water molecule to vibrate in the glassy phase compared to the rubbery phase is about 1×10^6 times longer. However, if the pore structure (diffusion space) is large enough, then this may have no effect. Ingredients can affect the local viscosity and thus mobility. Long chain polymers dissolved in the aqueous phase for a product in the rubbery region will lower the local mobility as was noted with the fiber addition to pizza sauce. Intermolecular association or interactions may contribute significantly to lowering the overall mobility of the molecules as was found by Tsoubeli et al.[46] using electron spin resonance (ESR).

With respect to physical pore size, theoretically, the diffusion of a small molecule such as water through a food domain is controlled by the molecule's size, the presence of other molecules in the vapor phase that the water molecules may collide with and the surrounding geometry, ie how tortuous the path is. Since we are dealing with foods, generally at 1 atm total pressure (0.1 MPa), with air present in the pores, the mean free path of the water molecule is very short because of the presence of the nitrogen and oxygen molecules. In addition, the overall flow is not like that of an inert gas (i.e. flow is not like N_2 passing through a bed of sand), thus the flow rate between domains of a multi-domain food cannot be easily predicted. Mathematical models for given geometries can be found in Geankopolis[47] and in Crank[48]. In a porous domain, molecules are allowed to transfer more quickly because of several mechanisms of moisture transfer (e.g. capillary action) along with liquid diffusion. In low porosity materials, liquid diffusion is the main method of moisture transport. The smaller the pore size in the matrix of the food domain, the slower the moisture migration. In addition, membranes, crystals, and lipids all contribute as barriers to moisture migration in a multi-domain system. The more crystals or lipid interferences in a system, the slower the diffusion of water.

It is important to note that the effective diffusion coefficient is dependent on both the surrounding structure and the solubility of the water in the matrix, the latter of which is governed by the GAB equation (Equation 9). In Fick's First Law (Equation 3) previously shown, the overall permeability of a matrix (k) is related to these factors through Equation (13):

$$k=DS$$

(13)

where D is the diffusion coefficient in the pore space (L^2/t (distance^2/time)) and S is the solubility. For the food systems under consideration here, the overall mass transfer is much more complex since it involves unsteady state diffusion (i.e. Δp decreases over time) which has an exponential dependence on moisture and the geometric dependence is L_o^2 not L_o (See Equation 14). For example, if the thickness of a filling is doubled, equilibration will take four times longer. In the case of moisture loss from a slab to the surroundings, the overall transfer is usually modeled as Equation (14):

$$\ln \Gamma = \ln \frac{m_e - m}{m_e - m_i} = \ln \frac{8}{\pi^2} - \frac{D_{eff} \pi^2}{4L_o^2} t \qquad (14)$$

where m_e = final equilibrium moisture (db); m_i = initial equilibrium moisture (db); m = moisture at time t; D_{eff} is the effective diffusivity in (L^2/t); L_o = distance from the center to the surface; Γ = unaccomplished moisture ratio (the amount of moisture remaining to change over the total amount of moisture that potentially changes). This shows that there will be a moisture gradient in the specific region as a function of time. Tütüncü and Labuza[49] showed that the above simple equation gives erroneous results in estimating D_{eff} and that at least 19 terms in the series expansion should be used to get the true D_{eff} (Equation 15) within a single matrix:

$$\Gamma = \frac{8}{\Pi^2} \sum_{n=0}^{n=19} \frac{1}{(2n+1)^2} \exp\left[\frac{-(2n+1)^2 \Pi^2 D_{eff}}{4L_o^2} t \right] \qquad (15)$$

Even this equation is difficult to use as it assumes either a spherical or slab dimension and no effect of the surrounding air space if the domain consists of particles like cereal flakes or raisins. Tütüncü and Labuza[49] showed in fact that the measure D_{eff} is very geometry dependent and thus any experimental design must take the final product configuration into consideration. More recently, finite element and finite difference computer techniques have been used to model non-simple geometric systems to obtain effective diffusivities[50].

The influence of pore structure on diffusion or permeability has been modeled by Geankopolis[47]. Unfortunately, there are few published values of diffusivity of water vapor or liquid transport in the pores of processed foods that would constitute a multi-domain system. Most values are from drying experiments which are generally not applicable as noted by Tütüncü and Labuza[49]. In general, the effective diffusivity values for moisture range from 10^{-9} to 10^{-12} m^2/s with the higher value applicable for porous foods like cereal and the lower value applicable to dense foods like raisins or dates[49,51]. It should be noted that the diffusion coefficient for water vapor in air is 2.4×10^{-5} m^2/sec and self-diffusion in liquid water is about 2×10^{-11} m^2/sec[52]. Thus, even the structure of a cereal flake slows down diffusion significantly which is an advantage to the creation of multi-domain foods.

Another way to slow diffusion between two domains is to create a diffusion barrier between them. Obviously , this has to be an edible barrier so the available barrier material is limiting. Biquet and Labuza[53] showed that chocolate is a good barrier to moisture because of the dispersion of fat (cocoa butter) throughout the matrix. This has limited applications to candies, confectioneries, frozen bakery goods and frozen desserts. For example, a chocolate layer on the inside of an ice cream cone will help reduce the moisture pickup and thereby maintain crispness of the cone during storage. Similarly a mixed starch-lipid layer can be used between the sauce and the crust to prevent crust sogginess in frozen pizzas[14]. Par frying the crust clogs the pores with oil and expands the structure, thereby reducing moisture pick up. Biquet and Labuza[53] summarized the basic properties needed for a good moisture barrier. The three properties that are important for moisture barrier selection are: (1) the barrier should have pores small enough to not allow water to pass through or to slow down the diffusion process, (2) the barrier should not contain structures similar to the permeant molecules and (3) the barrier must be adhesive to the food system. Fennema, Donhowe, and Kester[54] and Miller and Krochta[55] have given good reviews of the limitation of edible based films.

Conclusions & future work

Moisture migration in multi-domain food systems can lead to both physical and chemical changes that reduce the shelf-life of the food. The transfer of moisture is controlled by both thermodynamics and dynamics. Knowledge of these factors leads to several factors that can be used to reduce the rate of transfer of moisture. These include:

1. formulate the domains to as close to the same water activity as possible through the use of selected solutes

2. use ingredients with a high moisture content monolayer and high excess surface binding energy

3. mechanically treat the product to create as small a pore size and pore size distribution as possible

4. add ingredients that increase the local viscosity so as to inhibit diffusion and mobility

5. add an edible barrier between the domains.

For future studies dealing with moisture migration in multi-domain food systems, several issues still need to be addressed. State diagrams for the individual components of multi-domain systems would be useful for industrial applications. At the molecular level, NMR and MRI studies of water binding and flow should continue to be researched for a clearer understanding of moisture migration during storage. Next, flavor masking of humectants is important to keep the food system's flavor acceptability high while maintaining shelf-life. Finally, continued research in development of edible films will result in safe, effective, and organoleptically acceptable moisture barriers.

References

1 Sperling, L.H. (1986) *Introduction to Physical Polymer Science*, John Wiley & Sons, New York

2 Levine, H. and Slade L. (1988) 'Water as a Plasticizer: Physico-Chemical Aspects of Low-Moisture Polymeric Systems' in *Water Science Reviews* (Franks, F. ed.), vol. 3, pp.79-185, Cambridge University Press

3 Roos, Y. and Karel, M. (1991) 'Applying State Diagrams in Food Processing and Development' in *Food Technol.* 45(12),66-71,107

4 Roos, Y. (1995) 'Characterization of Food Polymers using State Diagrams' in *J. Food Eng.* 24, 229-360

5 Scott, W.J. (1957) 'Water Relation of Food Spoilage Microorganisms' in *Adv. Food Research* 7,83-127

6 Duckworth, R.B (1981) 'Solute Mobility in Relation to Water Content and Water Activity' in *Water Activity Influences on Food Quality* (Rockland, L.B. and Stewart, G.F., eds.), pp.295-317, Academic Press

7 Roos, Y. and Karel, M. (1991) 'Plasticizing Effect of Water on Thermal Behavior and Crystallization of Amorphous Food Models' in *J. Food Sci.* 56(1), 38-43

8 White, G.W. and Cakebread, S.H. (1966) 'The Glassy State in Certain Sugar-Containing Food Products' in *J. Food Technol.* 1,73-82

9 Hartel, R.W. (1993) 'Controlling Sugar Crystallization in Food Products' in *Food Technol.* 47(11), 99-107

10 Nelson, K.A. and Labuza, T.P. (1993) 'Glass Transition Theory and the Texture of Cereal Foods' in *The Glassy State in Foods* (Blanshard, J.M.V. and Lillford, P.J., eds.), pp.513-17, Nottingham University Press

11 Peleg, M. and Mannheim, C.H. (1977) 'The Mechanism of Caking of Powdered Onion' in *J. Food Proc. and Preserv.* 1,3-11

12 Tsourouflis, S. Flink, J.M., and Karel M. (1976) 'Loss of Structure in Freeze Dried Carbohydrates Solutions: Effect of Temperature, moisture and composition' in J. *Sci. Food Agr.* 27,507-519

13 Chuy, L.E. and Labuza, T.P. (1994) 'Caking and Stickiness of Dairy Based Food Powders as Related to Glass Transition' in *J. Food Sci.* 59(1),43-46

14 Kamper, S.L. and Fennema, O.R. (1985) 'Use of an Edible Film to Maintain Water Vapor Gradient in Foods' in *J. Food Sci.* 50(1), 382-4

15 Sauvageot, F. and Blond, G. (1991) 'Effect of Water Activity on Crispness of Breakfast Cereals' in *J. Texture Stud.* 22(4), 423-442

16 Rico-Peña, D.C. and Torres, J.A. (1990) 'Edible Methyl Cellulose Based Film as Moisture Impermeable Barriers in Sundae Ice Cream Cones' in *J. Food Sci.* 55(5), 1468-9

17 Katz, E.E. and Labuza, T.P. (1981) 'Effect of Water Activity on Sensory Crispness and Mechanical Deformation of Snack Food Products' in *J. Food Sci.* 46(1), 403-9

18 Hsieh F., Hu, L., Huff, H.E., and Peng, I.C. (1990) 'Effects of Water Activity on Textural Characteristics of Puffed Rice Cake' in *Lebensmittel Wiss. u-Technol.* 23(6), 471-3

19 Peleg, M. (1994) 'A Mathematical Model of Crunchiness/Crispness Loss in Breakfast Cereals' in *J. Texture Stud.* 25(4), 403-10

20 Vickers, Z. and Bourne, M.C. (1976) 'A Psychoacoustical Theory of Crispness' *J. Food Sci.* 41(2), 1158-64

21 Attenburrow, G.E., Davies, A.P., Goodband, R.M., and Ingman, S.J. (1992) 'The Fracture Behavior of Starch and Gluten in the Glassy State' in *J. Cereal Sci.* 16,1-12

22 Kirby, A.R., Clark, S.A., Parker, R., Smith, A.C. (1993) 'The Deformation and Failure Behavior of Wheat Starch Plasticized with Water and Polyoils' in *J. Mat. Sci.* 28, 5937-5942

23 Labuza, T.P. and Contreras-Medellin, R. (1981) 'Prediction of Moisture Protection Requirements for Foods' in *Cereal Foods World* 26(7), 335-343

24 Labuza, T.P. and Saltmarch, M. (1981) 'The Non-Enzymatic Browning Reaction as Affected by Water in Foods' in *Water Activity Influences in Food Quality* (Rockland, L.B. and Stewart, G.F., eds.), pp.605-650, AcedemicPress

25 Beuchat, L.R. (1981) 'Microbial Stability as Affected by Water Activity' in *Cereal Foods World* 26,345-349

26 Leistner, L. and Rodel, W. (1976) 'The Stability of Intermediate Moisture foods with Respect to Microorganisms' in *Intermediate Moisture Foods* (Davies, R., Birch, G.G., and Parker, K.J., eds.), pp.120-137, Applied Science

27 van den Berg, C. and Bruin, S. (1981) 'Water Activity and It's Estimation in Food Systems: Theoretical Aspects' in *Water Activity: Influences on Food Quality* (Rockland, L. and Stewart, G.F., eds.), pp.1-61, Academic Press

28 Sloan, A.E. and Labuza, T.P. (1976) 'Prediction of Water Activity Lowering Ability of Food Humectants at High a_w' in *J. Food Sci.* 41,532-535

29 Bone, D.P. (1969) 'Water Activity; Its Chemistry and Applications' in *Food Product Dev.* 3(5),81-94

30 Norrish, R.S. (1966) 'An Equation for the Activity Coefficients and Equilibrium Relative Humidities of Water in Confectionery Syrups' in *J. Food Technol* 1,25-39

31 Chirife, J. and Ferro-Fontan, C. (1980) 'Water Activity of Aqueous Lactulose Solutions' in *J. Food Sci.* 45(6), 1706-7

32 Miracco, J.L., Alzamora, S.M., Chirife, J. and Ferro-Fontán, C. (1981) 'On the Water Activity of Lactose Solution Potential Food Additive' in *J Food Sci.* 46(5), 1612-3

33 Chen, C.S. (1987) 'Calculation of Water Activity and Activity Coefficient of Sugar Solutions and Some Liquid Foods' in *Lebensmittel Wiss. u-Technol.* 20(2), 65-7

34 Alzaroma, S. and Chirife, J. (1984) 'The Water Activity of 1,3 and 2,3 Butylene Glycol Solutions' in *Lebensmittel Wiss. u.-Technol.* 17(5), 268-70

35 Chirife, J. and Ferro-Fontan, C. (1980) 'Prediction of Water Activity of Aqueous solutions in connection with Intermediate Moisture Foods; Experimental Investigation of the a_w lowering Behavior of Sodium Lactate and Some Related Compounds' in *J. Food Sci.* 45(4), 802-4

36 Gervais, P., Fasquel, J.P., and Molin, P. (1988) 'Water Relation of Fungal Spore Germination' in *Applied Micro. BioTechnol.* 29(6), 586-92

37 Labuza, T.P. (1984) *Moisture Sorption: Practical Aspects of Isotherm Measurement and Use*, AACC

38 Iglesias, H.A. and Chirife, J. (1982) *Handbook of Food Isotherms: Water Sorption Parameter for Food and Food Components*, Academic Press

39 Chen, P.L., Long, Z., Ruan, R.R., and Labuza, T.P. (1997) 'Nuclear Magnetic Resonance Studies of Water Mobility in Bread During Storage' in *Lebensmitten Wiss. u-Technol.* 30,178-183

40 Ruan, R. and Litchfield, J.B. (1992) 'Determination of Water Distribution and Mobility Inside Maize Kernels During Steeping Using Magnetic Resonance Imaging' in *Cereal Chem.* 69(1), 13-17

41 Schmidt, S.J. and Lai, H.M. (1991) 'Use of NMR and MRI to study Water Relation in Foods' *in Advances in Experimental and Medicine and Biology* (Levine, H. and Slade, L., eds), v.302, pp.405-52, Plenum Press

42 Umbach, S.L., Davis, E.A., Gordon, J., Callaghan, P.T. (1992) 'Water Self-diffusion and Dielectric Properties Determined for Starch-Gluten-Water Mixtures Heated by Microwave and by Conventional Methods' in *Cereal Chem.* 69(6), 637-42

43 Heil, J.R., Öezilgen, M., and McCarthy, M.J. (1993) 'Magnetic resonance Imaging Analysis of Water Migration and Void Formation in Baking Biscuits' in *AICHE Symposium Series* 89(297), 39-45

44 Jeffrey, K.R., Callaghan, C. and Xia, Y. (1994) 'The Measurement of Velocity Profiles: an Application of NMR Microscopy' in *Food Research Int.* 27(2), 199-201

45 Le Meste, M. (1995) 'Mobility of Small molecules in Low and Intermediate Moisture Foods' in *Food Preservation by Moisture Control* (Barbosa-Canavas, G.V. and Welti-Chanes, J., eds), pp.209-225, Technomic, Lancaster, PA

46 Tsoubeli, M.N., Davis, E.A., and Gordon, J. (1995) 'Dielectric Properties and Water Mobility for Heated Mixtures of Starch, Milk, Protein, and Water' in *Cereal Chem.* 72,64-69

47 Geankoplis, C.J. (1972) *Mass Transport Phenomena.* Holt, Reinhart, and Winston, New York

48 Crank, J. (1975) *Mathematics of Diffusion* (2nd ed.). Clavedon Press, Oxford England

49 Tütüncü, M.A. and Labuza, T.P. (1996) 'Effect of Geometry on the Effective Moisture Transfer Diffusion Coefficient' in *J. Food Eng.* 30,433-447

50 Hong, Y.C., Bakshi, A.S. and Labuza, T.P. (1986) 'Finite Element Modeling of Moisture Transfer During Storage of Mixed Multi Component Dried Foods' in *J. Food Sci.* 51(3),554-558

51 Gencturk, B., Bakshi, A.S., Hong, Y.C., and Labuza, T.P. (1986) 'Moisture Transfer Properties of Wild Rice' in *J. Food Proc. Eng.* 8, 243-53

52 *Handbook of Chemistry and Physics* (1958) Chemical Rubber Co.,40th ed., Cleveland, Ohio

53 Biquet, B. and Labuza, T.P. (1988) 'Evaluation of the Moisture Permeability Characteristics of Chocolate Films as an Edible Barrier' in *J. Food Sci.* 53(4), 989-97

54 Fennema, O., Donhowe, I.G., and Kester, J.J. (1993) 'Edible Films: Barriers to Moisture Migration in Frozen Foods' in *Food Australia* 45(11),521-52555 Miller, K.S. and Krochta, J.M. (1997) 'Oxygen and Aroma Barrier Properties of Edible films' in *Trends Food Sci. & Technol.* 8(7),228-237